

Cosmetic composition comprising a polymer

The present invention relates to a cosmetic composition comprising a particular polymer and intended for application to keratin materials of human beings, such as the skin, lips, eyelashes, eyebrows, nails and hair. The composition is intended more particularly for application to the skin or lips.

The composition according to the invention may be a makeup composition or a care composition for keratin materials, in particular for the skin and lips, and preferably a makeup composition.

The makeup composition may be a foundation, a lip makeup product (lipstick), an eyeshadow, a blusher, a concealer, an eyeliner, a body makeup product, a mascara, a nail varnish or a hair makeup product.

The care composition may be a face and body skincare product, in particular a sun product, or a skin colouring product (such as a self-tanning product). The composition may also be a hair product, especially for holding the hairstyle or for shaping the hair.

Makeup compositions are commonly used to give keratin materials an aesthetic colour. These makeup products generally contain oils, pigments and/or fillers and optionally additives, such as cosmetic or dermatological actives.

These compositions, when they are applied to

keratin materials, particularly to the skin, exhibit the disadvantage of transferring, i.e. of undergoing at least partial deposition, leaving marks, on certain substrates with which they may be contacted, and in particular a glass, cup, cigarette, item of clothing, or the skin. A consequence of this is mediocre persistence of the applied film, making it necessary regularly to renew the application of the lipstick or foundation composition. Moreover, the appearance of these unacceptable marks, particularly on blouse collars, may put certain women off using this type of makeup.

Furthermore, the sebum or perspiration excreted by the skin over the course of time also alters the properties of the makeup. In particular, sebum does not promote the adhesion of the makeup to the skin, and the transfer of the makeup is even greater, giving rise to a substantial loss of the makeup remaining on the skin.

When the makeup is in contact with water, such as during baths or showers, for example, or else with tears, the non-transfer properties of the makeup are also degraded.

"Transfer-free" skin makeup compositions are therefore sought which exhibit the advantage of forming a highly persistent deposit, especially in the presence of sebum or perspiration or water, and especially

compositions which do not undergo at least partial deposition onto substrates with which they are contacted (glass, clothing, cigarettes, fabrics).

For the purpose of enhancing the persistence of makeup products the use of film-forming polymers is known. For example, documents US 6,074,654 and WO 02/067877 propose the use of silicone resins.

It is therefore an object of the present invention to provide a new formulation pathway for a cosmetic product suitable for forming, on keratin materials, a deposit which exhibits good transfer resistance, especially in the presence of sebum or perspiration or water.

The inventors have discovered that it is possible to obtain such a composition by using a particular polymer.

More specifically, therefore, the present invention provides a cosmetic composition, in particular a keratin-material care or makeup composition, comprising a dispersion of particles, preferably solid particles, of a grafted acrylic polymer in a liquid fatty phase as described below, the said grafted acrylic polymer being obtainable by polymerizing at least one acidic ethylenic monomer, at least one non-acidic acrylic monomer and at least one macromonomer.

The invention also provides a method of

making up keratin materials which comprises applying to the keratin materials a composition as defined above.

The invention further provides for the use of a composition as defined above for obtaining a deposit, 5 in particular a makeup deposit, on keratin materials that has good transfer resistance, especially in the presence of sebum or perspiration or water.

The invention additionally provides for the use, in a cosmetic composition, of a dispersion of 10 particles (preferably solid particles) of a grafted acrylic polymer as defined above in dispersion in a liquid fatty phase for obtaining a deposit, in particular a makeup deposit, on keratin materials that exhibits good transfer resistance, especially in the 15 presence of sebum or perspiration or water.

The cosmetic composition according to the invention comprises a dispersion of particles, preferably solid particles, of a grafted acrylic polymer in a liquid fatty phase, the grafted acrylic 20 polymer being obtainable by polymerizing at least one acidic ethylenic monomer, at least one non-acidic acrylic monomer and at least one macromonomer.

The cosmetic composition according to the invention is a composition which is compatible with 25 keratin materials, and particularly with the skin.

The grafted acrylic polymer dispersion is free in particular of stabilizing polymers other than

the said grafted polymer, such as those described in EP 749 747, and the particles of grafted acrylic polymer are therefore not surface-stabilized by such additional stabilizing polymers. The grafted polymer is
5 therefore dispersed in the liquid fatty phase in the absence of additional stabilizer on the surface of the particles of the grafted polymer.

By grafted polymer is meant a polymer having a skeleton comprising at least one side chain which is
10 pendent or situated at the chain end, preferably pendent.

Advantageously, the grafted acrylic polymer comprises an acrylic skeleton which is insoluble in the said liquid fatty phase, and side chains bonded
15 covalently to the said skeleton and soluble in the said liquid fatty phase.

The grafted acrylic polymer is in particular a non-crosslinked polymer. In particular, the polymer is obtained by polymerizing monomers containing a
20 single polymerizable moiety.

Preferably, the grafted acrylic polymer is a film-forming polymer.

By "film-forming" polymer is meant a polymer suitable for forming, on its own or in the presence of
25 an auxiliary film-forming agent, a continuous film which adheres to a substrate, particularly to keratin materials.

The grafted acrylic polymer is obtainable in particular by free-radical polymerization in an organic polymerization medium:

- of at least one acidic ethylenic monomer, at least
- 5 one non-acidic acrylic monomer and, optionally, at least one additional, non-acidic, non-acrylic, vinyl monomer, to form an insoluble skeleton; and
- of at least one macromonomer containing a polymerizable end group for forming side chains, the
- 10 said macromonomer having a weight-average molecular mass of greater than or equal to 200, the amount of polymerized macromonomer representing from 0.05% to 20% by weight of the polymer.

The liquid fatty phase may contain the

15 organic polymerization medium.

The liquid organic dispersion medium, corresponding to the medium in which the grafted polymer is provided, may be identical to the polymerization medium.

20 However, the polymerization medium may be wholly or partly substituted by another liquid organic medium. This other liquid organic medium may be added after polymerization to the polymerization medium. The latter is then wholly or partly evaporated.

25 The liquid fatty phase may comprise organic liquid compounds other than those present in the dispersion medium. These other compounds are selected

such that the grafted polymer remains in the state of dispersion in the liquid fatty phase.

The organic liquid dispersion medium is present in the liquid fatty phase of the composition according to the invention owing to the introduction of the grafted polymer dispersion obtained into the composition.

The liquid fatty phase comprises, preferably on a majority basis, one or more liquid organic compounds (or oils) as defined below.

In particular, the liquid fatty phase is a liquid organic phase which is non-aqueous and water-immiscible at ambient temperature (25°C).

A "liquid organic compound" is a non-aqueous compound which is in the liquid state at ambient temperature (25°C) and which therefore flows under its own weight.

A "silicone compound" is a compound containing at least one silicon atom.

Among the liquid organic compounds or oils that may be present in the liquid organic dispersion medium, mention may be made of:

- liquid organic compounds, especially silicone-based or non-silicone-based, having a global solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)^{1/2} and preferably less than or equal to 17 (MPa)^{1/2},

- monoalcohols having a global solubility parameter according to the Hansen solubility space of less than or equal to $20 \text{ (MPa)}^{1/2}$, and
- mixtures thereof.

5 The global solubility parameter δ according to the Hansen solubility space is defined in the article "Solubility parameter values" by Eric A. Grulke in the work "Polymer Handbook", 3rd Edition, Chapter VII, p. 519-559, by the relationship:

10 $\delta = (d_D^2 + d_P^2 + d_H^2)^{1/2}$

in which

- d_D characterizes the London dispersion forces arising from the formation of dipoles induced during molecular impacts,
- 15 - d_P characterizes the Debye interaction forces between permanent dipoles, and
- d_H characterizes the forces of specific interactions (such as hydrogen bonding, acid/base, donor/acceptor, etc.).

20 The definition of solvents in the solubility space according to Hansen is described in the article by C. M. Hansen: "The three dimensional solubility parameters", J. Paint Technol. 39, 105 (1967).

 Among the liquid organic compounds,

25 especially silicone-based or non-silicone-based, having a global solubility parameter according to the Hansen solubility space of less than or equal to $18 \text{ (MPa)}^{1/2}$,

mention may be made of liquid fatty substances,
especially oils, which may be selected from natural or
synthetic, carbon-based, hydrocarbon-based, fluoro and
silicone oils, which are optionally branched, alone or
5 as a mixture.

An "oil" is any non-aqueous medium which is
liquid at ambient temperature (25°C) and atmospheric
pressure (760 mmHg) and is compatible with application
to the skin, mucosae (lips) and/or epidermal
10 derivatives (nails, eyebrows, eyelashes, hair).

Among these oils, mention may be made of
plant oils formed from fatty acid esters and from
polyols, in particular triglycerides, such as sunflower
oil, sesame oil or rapeseed oil, or esters derived from
15 acids or alcohols containing a long chain (i.e. a chain
containing from 6 to 20 carbon atoms), in particular
the esters of formula RCOOR' in which R represents a
higher fatty acid residue containing from 7 to 19
carbon atoms and R' represents a hydrocarbon-based
20 chain containing from 3 to 20 carbon atoms, such as
palmitates, adipates and benzoates, in particular
diisopropyl adipate.

Mention may also be made of linear, branched
and/or cyclic alkanes which may be volatile, and in
25 particular liquid paraffin, liquid petroleum jelly or
hydrogenated polyisobutylene, isododecane or "Isopars",
volatile isoparaffins. Mention may also be made of

esters, ethers and ketones.

Mention may also be made of silicone oils such as polydimethylsiloxanes and polymethylphenylsiloxanes, optionally substituted with aliphatic and/or aromatic groups, which are optionally fluorinated, or with functional groups such as hydroxyl, thiol and/or amine groups, and volatile silicone oils, which are especially cyclic.

In particular, mention may be made of volatile and/or non-volatile, optionally branched silicone oils.

The term "volatile oil" means any non-aqueous medium capable of evaporating from the skin or the lips in less than one hour, and especially having a vapour pressure, at ambient temperature and atmospheric pressure, ranging from 10^{-3} to 300 mmHg (0.13 Pa to 40 000 Pa).

As volatile silicone oils that may be used in the invention, mention may be made of linear or cyclic silicones containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. Mention may be made in particular of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof.

Among the non-volatile silicone oils that may be mentioned are non-volatile polydialkylsiloxanes, such as non-volatile polydimethylsiloxanes (PDMS); polydimethylsiloxanes comprising alkyl, alkoxy or phenyl groups, which are pendent or at the end of a silicone chain, these groups containing from 2 to 24 carbon atoms; phenyl silicones, for instance phenyl trimethicones, phenyl dimethicones, phenyl trimethylsiloxoxy diphenylsiloxanes, diphenyl dimethicones, diphenyl methyldiphenyltrisiloxanes and polymethylphenylsiloxanes; polysiloxanes modified with fatty acids (especially of C₈-C₂₀), fatty alcohols (especially of C₈-C₂₀) or polyoxyalkylenes (especially polyoxyethylene and/or polyoxypropylene); amino polysiloxanes; polysiloxanes containing hydroxyl groups; fluoro polysiloxanes comprising a fluorinated group that is pendent or at the end of a silicone chain, containing from 1 to 12 carbon atoms, all or some of the hydrogens of which are substituted by fluorine atoms; and mixtures thereof.

As non-silicone-based liquid organic compounds with a global solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)^{1/2}, mention may be made in particular of:

- linear, branched or cyclic esters containing at least 6 carbon atoms, especially 6 to 30 carbon atoms;
- ethers containing at least 6 carbon atoms, especially

6 to 30 carbon atoms; and

- ketones containing at least 6 carbon atoms,
especially 6 to 30 carbon atoms.

The expression "liquid monoalcohols having a
5 global solubility parameter according to the Hansen
solubility space of less than or equal to 20 (MPa)^{1/2}"
means aliphatic fatty liquid monoalcohols containing
from 6 to 30 carbon atoms, the hydrocarbon-based chain
not comprising a substitution group. Monoalcohols
10 according to the invention that may be mentioned
include oleyl alcohol, decanol and linoleyl alcohol.

Advantageously, the composition according to
the invention may comprise a volatile oil in an amount
ranging from 1% to 90% by weight, relative to the total
15 weight of the composition, and preferably ranging from
5% to 70% by weight.

The composition may comprise a non-volatile
oil in an amount ranging from 0.1% to 80% by weight,
relative to the total weight of the composition, and
20 preferably ranging from 3% to 50% by weight.

According to a first embodiment of the
invention, the liquid fatty phase may be a non-
silicone-based liquid fatty phase.

The term "non-silicone-based liquid fatty
25 phase" means a fatty phase comprising one or more
non-silicone-based liquid organic compound(s) or
oil(s), such as those mentioned above, the said

non-silicone compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or alternatively from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

The non-silicone-based liquid organic compounds may especially be selected from:

- 10 - non-silicone-based liquid organic compounds having a global solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)^{1/2},
- monoalcohols having a global solubility parameter according to the Hansen solubility space of less than
- 15 or equal to 20 (MPa)^{1/2}; and
- mixtures thereof.

The said non-silicone-based liquid fatty phase may thus optionally comprise silicone-based liquid organic compounds or oils, such as those

20 mentioned previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or alternatively ranging from 5% to 30% by weight, relative to the total weight of the liquid

25 fatty phase.

According to one particular embodiment of the invention, the non-silicone-based liquid fatty phase

does not contain any silicone-based liquid organic compounds or oils.

When the liquid fatty phase is a non-silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously carbon-based macromonomers as described below.

The term "non-silicone-based grafted polymer" means a grafted polymer predominantly containing a carbon-based macromonomer and optionally containing not more than 7% by weight of the total weight of the polymer, and preferably not more than 5% by weight, of silicone macromonomer, or even being free of silicone macromonomer.

According to a second embodiment of the invention, the liquid fatty phase may be a silicone-based liquid fatty phase.

The term "silicone-based liquid fatty phase" means a fatty phase comprising one or more silicone-based liquid organic compound(s) or silicone oil(s) such as those described previously, the said silicone compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or even from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

The silicone-based liquid organic compounds may especially be selected from:

- liquid organic compounds, which are especially non-silicone-based or silicone-based, with a global solubility parameter according to the Hansen solubility space of less than or equal to $18 \text{ (MPa)}^{1/2}$.

The said silicone-based liquid fatty phase may thus optionally comprise non-silicone-based liquid organic compounds or oils, as described previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or else ranging from 5% to 30% by weight, relative to the total weight of the liquid fatty phase.

According to one particular embodiment of the invention, the silicone-based liquid fatty phase contains no non-silicone-based liquid organic compounds.

When the liquid fatty phase is a silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously silicone-based macromonomers as described below.

In particular, when the liquid fatty phase is a silicone-based liquid fatty phase, the grafted polymer present in the composition is advantageously a silicone-based grafted polymer.

The term "silicone-based grafted polymer"

means a grafted polymer predominantly containing a silicone-based macromonomer optionally containing up to 7% by weight of the total weight of the polymer, and preferably up to 5% by weight, of carbon-based macromonomer, or even being free of carbon-based macromonomer.

The choice of monomers constituting the skeleton of the polymer, of macromonomers, the molecular weight of the polymer, and the proportion of the monomers and macromonomers may be made as a function of the liquid organic dispersion medium so as advantageously to obtain a dispersion of particles of grafted polymers, in particular a stable dispersion, this choice possibly being made by a person skilled in the art.

The term "stable dispersion" means a dispersion that is not liable to form a solid deposit or to undergo liquid/solid phase separation, especially after centrifugation, for example, at 4000 rpm for 15 minutes.

The grafted acrylic polymer forming the particles in dispersion thus comprises a skeleton that is insoluble in the said dispersion medium and a portion that is soluble in the said dispersion medium.

The grafted acrylic polymer may be a random polymer.

According to the invention, the term "grafted

acrylic polymer" means a polymer obtainable by free-radical polymerization:

- of one or more acrylic monomer(s), and optionally of one or more additional non-acrylic vinyl monomer(s);
- 5 - with one or more macromonomer(s), in an organic polymerization medium.

Preferably, the ethylenic acrylic or vinyl monomers are selected from monomers whose homopolymer is insoluble in the dispersion medium under
10 consideration, i.e. the homopolymer is in solid (or non-dissolved) form at a concentration of greater than or equal to 5% by weight at ambient temperature (20°C) in the said dispersion medium.

According to the invention, the expression
15 "macromonomer containing a polymerizable end group" means any polymer comprising on only one of its ends a polymerizable end group capable of reacting during the polymerization reaction with acrylic monomers and optionally the additional non-acrylic vinyl monomers
20 constituting the skeleton. The macromonomer makes it possible to form the side chains of the grafted acrylic polymer. The polymerizable group of the macromonomer may advantageously be an ethylenically unsaturated group capable of free-radical polymerization with the
25 monomers constituting the skeleton.

The term "carbon-based macromonomer" means a non-silicone-based macromonomer and especially an

oligomeric macromonomer obtained by polymerization of ethylenically unsaturated non-silicone-based monomer(s), and mainly by polymerization of acrylic and/or non-acrylic vinyl monomers.

5 The term "silicone-based macromonomer" means an organopolysiloxane macromonomer and in particular a polydimethylsiloxane macromonomer.

 Preferably, the macromonomer is selected from macromonomers whose homopolymer is soluble in the
10 dispersion medium under consideration, i.e. fully dissolved at a concentration of greater than or equal to 5% by weight and at ambient temperature in the said dispersion medium.

 Thus, the grafted acrylic polymer comprises a
15 skeleton (or main chain) consisting of a sequence of acrylic units resulting from the polymerization especially of one or more acrylic monomers and of side chains (or grafts) derived from the reaction of the macromonomers, the said side chains being covalently
20 bonded to the said main chain.

 The skeleton (or main chain) is insoluble in the dispersion medium under consideration, whereas the side chains (or grafts) are soluble in the said dispersion medium.

25 The insoluble skeleton of the grafted acrylic polymer contains at least one acidic ethylenic monomer and at least one non-acidic acrylic monomer.

The acidic ethylenic monomer may be selected from (meth)acrylic monomers containing at least one carboxylic, phosphoric or sulfonic acid function, non-(meth)acrylic vinyl monomers containing at least
5 one carboxylic, phosphoric or sulfonic acid function, and salts thereof.

In the present patent application, the term "non-acidic acrylic monomers" means monomers selected from (meth)acrylic acid esters (also known as
10 (meth)acrylates), and (meth)acrylic acid amides (also known as (meth)acrylamides) that do not contain an acidic group.

As an acidic ethylenic monomer mention may be made of (meth)acrylic acid, acrylamidopropanesulfonic
15 acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof. Preferably, the ethylenic monomer is (meth)acrylic acid.

The acidic ethylenic monomer may be present
20 in an amount ranging from 5% to 80% by weight, relative to the total weight of the polymer, preferably ranging from 10% to 70% by weight and preferentially ranging from 15% to 60% by weight.

According to one preferred embodiment of the
25 invention the acidic ethylenic monomer, or the grafted acrylic polymer, comprises a principal acidic monomer selected from (meth)acrylic acid and optionally an

additional acidic monomer different from (meth)acrylic acid, and salts thereof.

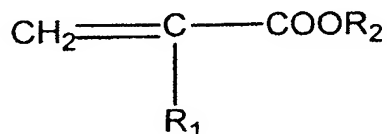
The additional acidic monomer may be selected from acrylamidosulfonic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof.

The (meth)acrylic acid may be present in an amount of at least 5% by weight, relative to the total weight of the polymer, in particular ranging from 5% to 80% by weight, preferably at least 10% by weight, in particular ranging from 10% by weight to 70% by weight, preferentially at least 15% by weight, in particular ranging from 15% to 60% by weight.

The additional acidic monomer may be present in an amount ranging from 0.1% to 20% by weight, relative to the total weight of the polymer, preferably ranging from 5% to 15% by weight.

As non-acidic acrylic monomers that may be used to form the insoluble skeleton of the polymer, mention may be made, alone or as a mixture, of the following monomers, and also the salts thereof:

-(i) the (meth)acrylates of formula:



in which:

- R₁ denotes a hydrogen atom or a methyl group;

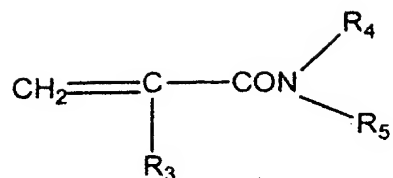
- R₂ represents a group selected from:

- a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms selected from O, N and S; and/or possibly comprising one or more substituents selected from -OH, halogen atoms (F, Cl, Br or I) and -NR'R'' with R' and R'', which may be identical or different, selected from linear or branched C₁-C₄ alkyls; and/or possibly being substituted with at least one polyoxyalkylene group, in particular with C₂-C₄ alkylene, especially polyoxyethylene and/or polyoxypropylene, the said polyoxyalkylene group consisting of a repetition of 5 to 30 oxyalkylene units;

- a cyclic alkyl group containing from 3 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms selected from O, N and S, and/or possibly comprising one or more substituents selected from OH and halogen atoms (F, Cl, Br or I).

Examples of R₂ that may be mentioned include the methyl, ethyl, propyl, butyl, isobutyl, methoxyethyl, ethoxyethyl, methoxypolyoxyethylene (350 EO), trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl or dimethylaminopropyl group;

-(ii) the (meth)acrylamides of formula:



in which:

- R₃ denotes a hydrogen atom or a methyl group;
- R₄ and R₅, which may be identical or different,
- 5. represent a hydrogen atom or a linear or branched alkyl group containing from 1 to 6 carbon atoms, which may comprise one or more substituents selected from -OH, halogen atoms (F, Cl, Br or I) and -NR'R'' with R' and R'', which may be identical or different, selected from
- 10 linear or branched C₁-C₄ alkyls; or
- R₄ represents a hydrogen atom and R₅ represents a 1,1-dimethyl-3-oxobutyl group.

As examples of alkyl groups that can constitute R₄ and R₅, mention may be made of n-butyl,

15 t-butyl, n-propyl, dimethylaminoethyl, diethylaminoethyl and dimethylaminopropyl.

Among these non-acidic acrylic monomers, those that may be mentioned most particularly are methyl, ethyl, propyl, butyl and isobutyl

20 (meth)acrylates; methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate,

25 2-hydroxyethyl acrylate; dimethylaminopropylmeth-

acrylamide; and the salts thereof; and mixtures thereof.

Preferably, the non-acidic acrylic monomers are selected from methyl acrylate, methoxyethyl
5 acrylate, methyl methacrylate, 2-hydroxyethyl methacrylate, (meth)acrylic acid and dimethylaminoethyl methacrylate, and mixtures thereof.

Advantageously, the non-acidic acrylic monomer may be selected from C₁-C₃ alkyl
10 (meth)acrylates.

The grafted acrylic polymer as defined above may be obtainable, moreover, by polymerization in the presence of one or more additional non-acidic non-acrylic vinyl monomers.

15 Among the additional non-acidic non-acrylic vinyl monomers that may be mentioned are:

- vinyl esters of formula: $R_6\text{-COO-CH=CH}_2$
in which R₆ represents a linear or branched alkyl group containing from 1 to 6 carbon atoms, or a cyclic alkyl
20 group containing from 3 to 6 carbon atoms and/or an aromatic group, for example of benzene, anthracene or naphthalene type;
- non-acidic non-acrylic vinyl monomers comprising at least one tertiary amine function, such as
25 2-vinylpyridine or 4-vinylpyridine;
- and mixtures thereof.

Advantageously, the grafted acrylic polymer

contains from 50% to 100% by weight, preferably from 55% to 100% by weight (in particular from 55% to 95% by weight), preferentially from 60% to 100% by weight (in particular from 60% to 90% by weight) of acrylic monomer(s) relative to the total weight of the mixture of acrylic monomers + optional non-acrylic vinyl monomers.

Among the salts, those that may be mentioned are those obtained by neutralization of acidic moieties with inorganic bases such as sodium hydroxide, potassium hydroxide or ammonium hydroxide, or organic bases such as alkanolamines, for instance monoethanolamine, diethanolamine, triethanolamine or 2-methyl-2-amino-1-propanol.

Mention may also be made of the salts formed by neutralization of tertiary amine units, for example using a mineral or organic acid. Among the mineral acids that may be mentioned are sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid and boric acid. Among the organic acids that may be mentioned are acids comprising one or more carboxylic, sulfonic or phosphonic groups. They may be linear, branched or cyclic aliphatic acids, or alternatively aromatic acids. These acids may also comprise one or more heteroatoms selected from O and N, for example in the form of hydroxyl groups. Acetic acid or propionic acid, terephthalic acid, and citric acid

and tartaric acid may especially be mentioned.

According to one embodiment of the invention, the grafted acrylic polymer contains no additional non-acrylic vinyl monomers as described above. In this
5 embodiment, the insoluble skeleton of the grafted acrylic polymer is formed solely from acrylic monomers as described previously.

It is understood that these non-polymerized ethylenic, acrylic or vinyl monomers may be soluble in
10 the dispersion medium under consideration, but the polymer formed with these monomers is insoluble in the dispersion medium.

The macromonomers comprise at one of the ends of the chain a polymerizable end group capable of
15 reacting during the polymerization with the acrylic monomers and optionally the additional vinyl monomers, to form the side chains of the grafted acrylic polymer. The said polymerizable end group may in particular be a vinyl or (meth)acrylate (or (meth)acryloyl) group, and
20 preferably a (meth)acrylate group.

The macromonomers are preferably selected from macromonomers whose homopolymer has a glass transition temperature (T_g) of less than or equal to 25°C , especially ranging from -100°C to 25°C and
25 preferably ranging from -80°C to 0°C .

The macromonomers have a weight-average molecular mass of greater than or equal to 200,

preferably greater than or equal to 300, preferentially greater than or equal to 500 and more preferentially greater than 600.

Preferably, the macromonomers have a weight-average molecular mass (M_w) ranging from 200 to 100 000, preferably ranging from 500 to 50 000, preferentially ranging from 800 to 20 000, more preferentially ranging from 800 to 10 000 and even more preferentially ranging from 800 to 6000.

In the present patent application, the weight-average (M_w) and number-average (M_n) molar masses are determined by liquid gel permeation chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

Carbon-based macromonomers that may in particular be mentioned include:

-(i) homopolymers and copolymers of linear or branched C_8 - C_{22} alkyl (meth)acrylate, containing a polymerizable end group selected from vinyl or (meth)acrylate groups, among which mention may be made in particular of: poly(2-ethylhexyl acrylate) macromonomers with a mono(meth)acrylate end group; poly(dodecyl acrylate) or poly(dodecyl methacrylate) macromonomers with a mono(meth)acrylate end group; poly(stearyl acrylate) or poly(stearyl methacrylate) macromonomers with a mono(meth)acrylate end group.

Such macromonomers are described in particular in the patents EP 895 467 and EP 96 459, and in the article by Gillman K.F., Polymer Letters, Vol 5, pages 477-481 (1967).

- 5 Mention may be made in particular of macromonomers based on poly(2-ethylhexyl acrylate) or poly(dodecyl acrylate) with a mono(meth)acrylate end group;
- (ii) polyolefins containing an ethylenically
- 10 unsaturated end group, in particular containing a (meth)acrylate end group. Examples of such polyolefins that may be mentioned in particular include the following macromonomers, it being understood that they have a (meth)acrylate end group: polyethylene
- 15 macromonomers, polypropylene macromonomers, macromonomers of polyethylene/polypropylene copolymer, macromonomers of polyethylene/polybutylene copolymer, polyisobutylene macromonomers; polybutadiene macromonomers; polyisoprene macromonomers;
- 20 polybutadiene macromonomers; poly(ethylene/butylene)-polyisoprene macromonomers.

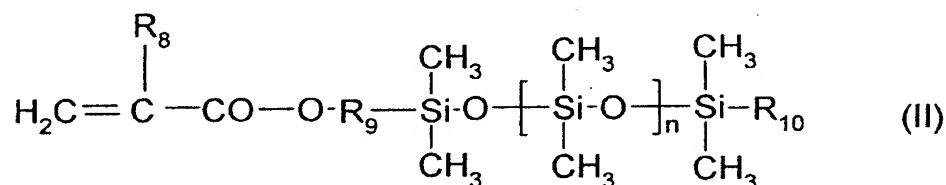
Such macromonomers are described in particular in US 5,625,005, which mentions ethylene/butylene and ethylene/propylene macromonomers

25 containing a (meth)acrylate reactive end group.

Mention may be made in particular of the poly(ethylene/butylene) methacrylate such as that sold

under the name Kraton Liquid L-1253 by Kraton Polymers.

Silicone-based macromonomers that may be mentioned in particular include polydimethylsiloxanes with a mono(meth)acrylate end group, and especially
 5 those of formula (II) below:



in which R_8 denotes a hydrogen atom or a methyl group;
 R_9 denotes a divalent hydrocarbon-based group containing from 1 to 10 carbon atoms and optionally contains one
 10 or two ether bonds $-\text{O}-$; R_{10} denotes an alkyl group containing from 1 to 10 carbon atoms and especially from 2 to 8 carbon atoms; n denotes an integer ranging from 1 to 300, preferably ranging from 3 to 200 and preferentially ranging from 5 to 100.

15 Silicone-based macromonomers that may be used include monomethacryloxypropyl polydimethylsiloxanes such as those sold under the name PS560-K6 by the company United Chemical Technologies Inc. (UCT) or under the name MCR-M17 by the company Gelest Inc.

20 Preferably, the polymerized macromonomer (constituting the side chains of the grafted polymer) represents from 0.1% to 15% by weight of the total weight of the polymer, preferably from 0.2% to 10% by weight and more preferably from 0.3% to 8% by weight.

As particularly preferred grafted acrylic polymer dispersed in a non-silicone-based liquid fatty phase, it is possible to use those obtained by polymerization:

- 5 - of methyl acrylate/acrylic acid monomers and of a polyethylene/polybutylene macromonomer with a methacrylate end group (especially Kraton L-1253), in particular in isododecane.

As particularly preferred grafted acrylic
10 polymer dispersed in a silicone-based liquid fatty phase, it is possible to use those obtained by polymerization:

- of methyl acrylate, acrylic acid and the monomethacryloyloxypropyl polydimethylsiloxane
15 macromonomer with a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane.

The weight-average molecular mass (M_w) of the grafted polymer is preferably between 10 000 and
20 300 000, especially between 20 000 and 200 000 and better still between 25 000 and 150 000.

By virtue of the abovementioned characteristics, in a given organic dispersion medium, the polymers have the capacity of folding over on
25 themselves, thus forming particles of substantially spherical shape, the periphery of these particles having the deployed side chains, which ensure the

stability of these particles. Such particles resulting from the characteristics of the grafted polymer have the particular feature of not agglomerating in the said medium and thus of being self-stabilized and of forming
5 a particularly stable polymer particle dispersion.

In particular, the grafted acrylic polymers of the dispersion are capable of forming nanometre-sized particles, with a mean size ranging from 10 to 400 nm and preferably from 20 to 200 nm.

10 As a result of this very small size, the grafted polymer particles in dispersion are particularly stable and therefore have little susceptibility to form agglomerates.

The dispersion of grafted polymer may thus be
15 a dispersion that is stable and does not form sediments when it is placed at ambient temperature (25°C) for an extended period (for example 24 hours).

Preferably, the dispersion of grafted polymer particles has a solids content (or dry extract) of
20 polymer of from 40% to 70% by weight of solids and especially from 45% to 65% by weight.

The dispersion of grafted polymer particles may be prepared by a process comprising a free-radical copolymerization step, in an organic polymerization
25 medium, of one or more acrylic monomers as defined above with one or more macromonomers as defined above.

As mentioned previously, the liquid organic

dispersion medium may be identical to or different from the polymerization medium.

The copolymerization may be performed conventionally in the presence of a polymerization initiator. The polymerization initiators may be free-radical initiators. In general, such a polymerization initiator may be selected from organic peroxide compounds such as dilauroyl peroxide, dibenzoyl peroxide or tert-butyl peroxy-2-ethylhexanoate; diazo compounds such as azobisisobutyronitrile or azobisdimethylvaleronitrile.

The reaction may also be initiated using photoinitiators or with radiation such as UV or neutrons, or with plasma.

In general, to perform this process, at least a portion of the organic polymerization medium, a portion of the additional acrylic and/or vinyl monomers, which will constitute the insoluble skeleton after polymerization, all of the macromonomer (which will constitute the side chains of the polymer) and a portion of the polymerization initiator are introduced into a reactor whose size is suitable for the amount of polymer to be prepared. At this stage of introduction, the reaction medium forms a relatively homogeneous medium.

The reaction medium is then stirred and heated up to a temperature to obtain polymerization of

the monomers and macromonomers. After a certain time, the initially homogeneous and clear medium leads to a dispersion of milky appearance. A mixture consisting of the remaining portion of monomers and of polymerization initiator is then added. After an adequate time during which the mixture is heated with stirring, the medium stabilizes in the form of a milky dispersion, the dispersion comprising polymer particles stabilized in the medium in which they have been created, the said
10 stabilization being due to the presence, in the polymer, of side chains that are soluble in the said dispersion medium.

The grafted polymer described above may be present in the composition according to the invention
15 in an amount ranging from 0.1% to 70% by weight relative to the total weight of the composition, preferably ranging from 0.5% to 50% by weight and preferentially ranging from 1% to 40% by weight.

The composition according to the invention
20 may comprise one or more colorants selected from water-soluble dyes and pulverulent colorants such as pigments, nacles and flakes, which are well known to the person skilled in the art. The colorants may be present in the composition in an amount ranging from
25 0.01% to 50% by weight, relative to the weight of the composition, preferably from 0.01% to 30% by weight.

By pigments are meant white or coloured,

mineral or organic particles of any form which are insoluble in the physiological medium and are intended for colouring the composition.

Nacres are irridescent particles of any form, produced in particular by certain molluscs within their shell, or else synthesized.

The pigments may be white or coloured, mineral and/or organic. Among mineral pigments mention may be made of titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders such as aluminium powder and copper powder.

Among organic pigments mention may be made of carbon black, D & C pigments, and lakes based on cochineal carmine, barium, strontium, calcium and aluminium.

Mention may also be made of effect pigments, such as particles comprising an organic or mineral, natural or synthetic substrate, for example glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, the said substrate being bare or covered with metallic substances such as aluminium, gold, silver, platinum, copper, bronze, or with metal oxides such as titanium dioxide, iron oxide, chromium oxide and mixtures thereof.

The nacreous pigments may be selected from white nacreous pigments such as titanium-coated mica, or bismuth oxychloride, coloured nacreous pigments such as titanium mica coated with iron oxides, titanium mica
5 coated with, in particular, ferric blue or chromium oxide, titanium mica coated with an organic pigment of the aforementioned type, and also nacreous pigments based on bismuth oxychloride. Use may also be made of interference pigments, especially liquid-crystal
10 pigments or multilayer pigments.

The grafted polymer in dispersion makes it possible, surprisingly, to disperse the pulverulent colorants, such as the pigments and nacles, readily in the composition.

15 The invention accordingly further provides a foundation composition comprising a dispersion of particles of grafted acrylic polymer in a liquid fatty phase, as described above, and at least one colorant, especially pigments and nacles, or any other filler
20 having an optical effect.

The water-soluble dyes are, for example, beetroot juice and methylene blue.

The composition according to the invention may further comprise one or more fillers, in particular
25 in an amount ranging from 0.01% to 50% by weight, relative to the total weight of the composition, preferably ranging from 0.01% to 30% by weight. By

fillers are meant particles of any shape, colourless or white, mineral or synthetic, which are insoluble in the medium of the composition irrespective of the temperature at which the composition is manufactured.

- 5 These fillers serve in particular to modify the rheology or texture of the composition.

The fillers may be mineral or organic fillers of any form, platelet-like, spherical or oblong, irrespective of the crystallographic form (for example, 10 leaflet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powders (Orgasol® from Atochem), poly- β -alanine powders and polyethylene powders, powders of polymers of tetrafluoroethylene (Teflon®), lauroyllysine, 15 starch, boron nitride, hollow polymeric microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industries), and of acrylic acid copolymers (Polytrap® from Dow Corning), and silicone resin microbeads (Tospearls® from Toshiba, 20 for example), particles of elastomeric organopolysiloxanes, precipitated calcium carbonate, magnesium carbonate and bicarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, metal soaps 25 derived from organic carboxylic acids having 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, for example zinc stearate, magnesium stearate or lithium

stearate, zinc laurate and magnesium myristate.

The composition according to the invention may additionally comprise at least one fatty substance which is solid at ambient temperature and is selected
5 in particular from waxes, pasty fats, gums and mixtures thereof. These fatty substances may be animal, vegetable, mineral or synthetic in origin.

By pasty fat is meant a lipophilic fatty compound comprising a liquid fraction and a solid
10 fraction at a temperature of 23°C.

The said pasty compound preferably has a hardness at 20°C ranging from 0.001 to 0.5 MPa and preferably from 0.002 to 0.4 MPa.

The hardness is measured according to a
15 method of penetration of a probe into a sample of compound and in particular using a texture analyser (for example the TA-XT2i instrument from Rheo) equipped with a stainless-steel spindle 2 mm in diameter. The hardness measurement is performed at 20°C at the centre
20 of five samples. The spindle is introduced into each sample at a pre-speed of 1 mm/s and then at a measuring speed of 0.1 mm/s, the penetration depth being 0.3 mm. The hardness value obtained is that of the maximum peak.

25 The liquid fraction of the pasty compound measured at 23°C preferably represents 9% to 97% by weight of the compound. This liquid fraction at 23°C

preferably represents between 15% and 85% and more preferably between 40% and 85% by weight. The liquid fraction by weight of the pasty compound at 23°C is equal to the ratio of the heat of fusion consumed at 23°C to the heat of fusion of the pasty compound.

The heat of fusion of the pasty compound is the enthalpy consumed by the compound to change from the solid state to the liquid state. The pasty compound is said to be in the solid state when all of its mass is in solid crystalline form. The pasty compound is said to be in the liquid state when all of its mass is in liquid form.

The heat of fusion of the pasty compound is equal to the area under the curve of the thermogram obtained using a differential scanning calorimeter (DSC), such as the calorimeter sold under the name MDSC 2920 by the company TA Instrument, with a temperature rise of 5 or 10°C per minute, according to standard ISO 11357-3:1999. The heat of fusion of the pasty compound is the amount of energy required to make the compound change from the solid state to the liquid state. It is expressed in J/g.

The heat of fusion consumed at 23°C is the amount of energy absorbed by the sample to change from the solid state to the state that it has at 23°C, consisting of a liquid fraction and a solid fraction.

The liquid fraction of the pasty compound,

measured at 32°C, preferably represents from 30% to 100% by weight of the compound, preferably from 80% to 100% and more preferably from 90% to 100% by weight of the compound. When the liquid fraction of the pasty
5 compound measured at 32°C is equal to 100%, the temperature of the end of the melting range of the pasty compound is less than or equal to 32°C.

The liquid fraction of the pasty compound measured at 32°C is equal to the ratio of the heat of
10 fusion consumed at 32°C to the heat of fusion of the pasty compound. The heat of fusion consumed at 32°C is calculated in the same manner as the heat of fusion consumed at 23°C.

A wax in the sense of the present invention
15 is a lipophilic compound which is solid at ambient temperature (25°C) and exhibits a reversible solid/liquid state change, having a melting point of greater than or equal to 30°C and possibly up to 120°C.

The melting point of the wax can be measured
20 by means of a differential scanning calorimeter (DSC), an example being the calorimeter sold under the name DSC 30 by the Mettler Company.

The waxes may be hydrocarbon waxes, fluoro waxes and/or silicone waxes and may be vegetable,
25 mineral, animal and/or synthetic in origin. In particular the waxes exhibit a melting temperature of greater than or equal to 30°C and more preferably

greater than 45°C.

As a wax which can be used in the composition of the invention, mention may be made of beeswax, carnauba wax or candelilla wax, paraffin, 5 microcrystalline waxes, ceresine or ozokerite; synthetic waxes such as polyethylene or Fischer-Tropsch waxes, and silicone waxes such as alkyl or alkoxy dimethicones having 16 to 45 carbon atoms.

The gums are generally high molecular weight 10 polydimethylsiloxanes (PDMS) or cellulose gums or polysaccharides and the pasty fats are generally hydrocarbon-based compounds such as lanolins and derivatives thereof or else PDMS.

The identity and amount of the solid 15 substances are a function of the desired mechanical properties and textures. As an indication, the composition may contain from 0.1% to 50% by weight of waxes, relative to the total weight of the composition, and more preferably from 1% to 30% by weight.

20 The composition may therefore comprise water or a mixture of water and hydrophilic organic solvent(s), such as alcohols, and especially linear or branched lower monoalcohols having 2 to 5 carbon atoms such as ethanol, isopropanol or n-propanol, and polyols 25 such as glycerol, diglycerol, propylene glycol, sorbitol, butylene glycol, pentylene glycol, hexylene glycol and polyethylene glycols.

The water or the mixture of water and hydrophilic organic solvents may be present in the composition according to the invention in an amount ranging from 0.1% to 95% by weight, relative to the total weight of the composition, and preferably ranging from 1% to 80%, and more preferably ranging from 10% to 80% by weight.

The composition according to the invention may further comprise ingredients commonly used in cosmetology, such as vitamins, moisturizers, thickeners, trace elements, softeners, sequesterants, perfumes, alkalifying or acidifying agents, preservatives, plasticizers, sunscreens, surfactants, antioxidants, hair loss preventatives, anti-dandruff agents, propellants, or mixtures thereof.

The person skilled in the art will of course take care to select this or these optional additional compounds, and/or their amount, such that the advantageous properties of the corresponding composition according to the invention are not, or not substantially, adversely affected by the intended addition.

The composition according to the invention may be present in particular in the form of a suspension, dispersion, solution, gel, emulsion, particularly an oil-in-water (O/W) or water-in-oil (W/O) emulsion, or multiple (W/O/W or polyol/O/W or

O/W/O) emulsion, in the form of a cream, paste or mousse, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multiphase lotion, or a spray, powder or paste. The composition may be
5 anhydrous: for example, it may comprise a stick or an anhydrous paste. The composition may be a composition which is used without rinsing.

A person skilled in the art may select the appropriate galenical form, and also the method of
10 preparing it, on the basis of his or her general knowledge, taking into account firstly the nature of the constituents used, especially their solubility in the vehicle, and secondly the intended application of the composition.

15 According to another aspect, the invention also relates to a cosmetic assembly comprising:

- i) a container delimiting at least one compartment, the said container being closed by a closing member; and
- 20 ii) a composition disposed within the said compartment, the composition being in accordance with the invention.

The container may be in any appropriate form. It may especially be in the form of a bottle, a tube, a
25 jar, a case, a box, a sachet or a carton.

The closing member may be in the form of a removable stopper, a lid, a cap, a tear-off strip or a

capsule, especially of the type comprising a body
attached to the container and a cover cap articulated
on the body. It may also be in the form of a member for
selectively closing the container, especially a pump, a
5 valve or a flap valve.

The container may be combined with an
applicator, especially in the form of a brush
comprising an arrangement of bristles maintained by a
twisted wire. Such a twisted brush is described
10 especially in patent US 4,887,622. It may also be in
the form of a comb comprising a plurality of
application members, obtained especially by moulding.
Such combs are described, for example, in patent
FR 2 796 529. The applicator may be in the form of a
15 fine brush, as described, for example, in patent
FR 2 722 380. The applicator may be in the form of a
block of foam or of elastomer, a felt or a spatula. The
applicator may be free (tuft or sponge) or securely
fastened to a rod borne by the closing member, as
20 described, for example, in patent US 5,492,426. The
applicator may be securely fastened to the container,
as described, for example, in patent FR 2 761 959.

The product may be contained directly in the
container, or indirectly. By way of example, the
25 product may be arranged on an impregnated support,
especially in the form of a wipe or a pad, and arranged
(individually or in plurality) in a box or in a sachet.

Such a support incorporating the product is described, for example, in patent application WO 01/03538.

The closing member may be coupled to the container by screwing. Alternatively, the coupling
5 between the closing member and the container is done other than by screwing, especially via a bayonet mechanism, by snap-fastening, gripping, welding, adhesive bonding or by magnetic attraction. The term "snap-fastening" in particular means any system
10 involving the crossing of a bead or cord of material by elastic deformation of a portion, especially of the closing member, followed by return to the elastically unconstrained position of the said portion after the crossing of the bead or cord.

15 The container may be at least partially made of thermoplastic material. Examples of thermoplastic materials that may be mentioned include polypropylene or polyethylene.

Alternatively, the container is made of non-
20 thermoplastic material, especially glass or metal (or alloy).

The container may have rigid walls or deformable walls, especially in the form of a tube or a tubular bottle.

25 The container may comprise means for distributing or facilitating the distribution of the composition. By way of example, the container may have

deformable walls so as to allow the composition to exit
in response to a positive pressure inside the
container, this positive pressure being caused by
elastic (or non-elastic) squeezing of the walls of the
5 container. Alternatively, especially when the product
is in the form of a stick, the product may be driven
out by a piston mechanism. Still in the case of a
stick, especially of makeup product (lipstick,
foundation, etc.), the container may comprise a
10 mechanism, especially a rack mechanism, a threaded-rod
mechanism or a helical groove mechanism, and may be
capable of moving a stick in the direction of the said
aperture. Such a mechanism is described, for example,
in patent FR 2 806 273 or in patent FR 2 775 566. Such
15 a mechanism for a liquid product is described in patent
FR 2 727 609.

The container may consist of a carton with a
base delimiting at least one housing containing the
composition, and a lid, especially articulated on the
20 base, and capable of at least partially covering the
said base. Such a carton is described, for example, in
patent application WO 03/018423 or in patent
FR 2 791 042.

The container may be equipped with a drainer
25 arranged in the region of the aperture of the
container. Such a drainer makes it possible to wipe the
applicator and possibly the rod to which it may be

securely fastened. Such a drainer is described, for example, in patent FR 2 792 618.

The composition may be at atmospheric pressure inside the container (at room temperature) or
5 pressurized, especially by means of a propellant gas (aerosol). In the latter case, the container is equipped with a valve (of the type used for aerosols).

The content of the patents or patent applications mentioned above is incorporated by
10 reference into the present patent application.

The invention will now be described in more detail in the light of the following examples, which are given by way of illustration and not of limitation.

The present examples illustrate the
15 preparation of polymers in accordance with the invention that are suitable for forming a dispersion of particles in an organic medium under consideration.

In these examples, following preparation of the said dispersion, the weight-average (M_w) and
20 number-average (M_n) molar masses of the polymer, the glass transition temperature of the polymer, the solids content (or dry extract) of the dispersion and the size of the polymer particles are determined.

The weight-average (M_w) and number-average
25 (M_n) molar masses are determined by liquid gel-permeation chromatography (THF solvent, calibration curve established with linear polystyrene standards,

refractometric detector).

The measurement of the glass transition temperature (T_g) is performed according to standard ASTM D3418-97, by differential thermal analysis (DSC "Differential Scanning Calorimetry") on a calorimeter, over a temperature range between -100°C and $+150^{\circ}\text{C}$, at a heating rate of $10^{\circ}\text{C}/\text{minute}$ in 150 μl aluminium crucibles.

The crucibles are prepared in the following manner: 100 μl of the dispersion obtained are introduced into a 150 μl aluminium crucible and the solvent is allowed to evaporate over 24 hours at ambient temperature and at 50% relative humidity. The operation is repeated and the crucible is then introduced into a Mettler DSC30 calorimeter.

The solids content (or dry extract), i.e. the amount of non-volatile matter, may be measured in various ways: mention may be made, for example, of the methods by oven-drying or the methods by drying by exposure to infrared radiation.

The solids content is preferably measured by heating the sample with infrared rays with a wavelength of from 2 μm to 3.5 μm . The substances contained in the composition that have a high vapour pressure evaporate under the effect of this radiation. Measuring the weight loss of the sample makes it possible to determine the dry extract of the composition. These

measurements are performed using an LP16 commercial infrared desiccator from Mettler. This technique is fully described in the documentation for the instrument supplied by Mettler.

5 The measuring protocol is as follows: about 1 g of the composition is spread onto a metal cup. After introducing this cup into the desiccator, it is subjected to a nominal temperature of 120°C for an hour. The wet mass of the sample, corresponding to the
10 initial mass, and the dry mass of the sample, corresponding to the mass after exposure to the radiation, are measured using a precision balance.

 The solids content is calculated in the following manner:

15 $\text{dry extract} = 100 \times (\text{dry mass}/\text{wet mass}).$

 The particle sizes may be measured by various techniques: mention may be made in particular of light-scattering techniques (dynamic and static), Coulter counter methods, sedimentation rate measurements
20 (related to the size via Stokes' law) and microscopy. These techniques make it possible to measure a particle diameter and, for some of them, a particle size distribution.

 The sizes and size distributions of the
25 particles in the compositions according to the invention are preferably measured by static light scattering using a commercial granulometer such as the

MasterSizer 2000 from Malvern. The data are processed on the basis of the Mie scattering theory. This theory, which is exact for isotropic particles, makes it possible to determine an "effective" particle diameter in the case of non-spherical particles. This theory is described especially in the work by Van de Hulst, H.C., "Light Scattering by Small Particles", Chapters 9 and 10, Wiley, New York, 1957.

The composition is characterized by its mean "effective" diameter by volume $D[4.3]$, defined in the following manner:

$$D[4.3] = \frac{\sum_i V_i \cdot d_i}{\sum_i V_i}$$

in which V_i represents the volume of the particles with an effective diameter d_i . This parameter is described especially in the technical documentation of the granulometer.

The measurements are performed at 25°C on a dilute particle dispersion, obtained from the composition in the following manner: 1) dilution by a factor of 100 with water, 2) homogenization of the solution, 3) standing of the solution for 18 hours, 4) recovery of the whitish uniform supernatant.

The "effective" diameter is obtained by taking a refractive index of 1.33 for water and a mean refractive index of 1.42 for the particles.

The invention is illustrated in more detail

by the examples described below.

Example 1:

This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and the macromonomer corresponding to a polyethylene/polybutylene copolymer (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 14 g of methyl acrylate, 10 g of acrylic acid, 16 g of macromonomer of the polyethylene/polybutylene copolymer type containing methacrylate end groups (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 130 g of methyl acrylate, 30 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour.

Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of

polymer thus prepared in isododecane.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass $M_w = 175\,294$
- 5 - number-average molecular mass $M_n = 28\,265$
- polydispersity index (M_w/M_n) = 6.2
- theoretical dry extract: 54.9% in isododecane
- particle size: 85 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

10 The grafted polymer comprises 8% by weight of macromonomer relative to the weight of the polymer.

 The stability of the dispersion obtained is demonstrated by implementing the following stability protocol: 8 ml of dispersion produced are placed in a
15 haemolysis tube and centrifuged at 4000 rpm for 15 minutes using a Jouan C100-S5 centrifuge. After 15 minutes, it is found that there is no phase separation, thereby demonstrating the dispersion is stable.

20 **Example 2:**

 This example illustrates the preparation of a polymer forming a dispersion of particles in a silicone-based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and
25 a monomethacryloyloxypropyl polydimethylsiloxane macromonomer having a weight-average molecular weight of 5000, sold under the name MCR-M17 by Gelest Inc.

200 g of heptane, 200 g of
decamethylcyclopentasiloxane, 26 g of methyl acrylate,
14 g of monomethacryloyloxypropyl polydimethylsiloxane
MCR-M17 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate
5 (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated to
90°C over 1 hour. After 15 minutes at 90°C, a change is
observed in the appearance of the reaction medium,
which passes from a transparent appearance to a milky
10 appearance. Heating with stirring is continued for a
further 15 minutes, and a mixture consisting of 120 g
of methyl acrylate, 40 g of acrylic acid and 2 g of
Trigonox 21S is then added dropwise over 1 hour. Next,
the mixture is heated for 4 hours at 90°C and the
15 heptane is then distilled from the reaction medium.

The outcome of this distillation operation is
a stable dispersion of particles of polymer thus
prepared in decamethylcyclopentasiloxane.

The grafted polymer comprises 7% by weight of
20 macromonomer (and hence of side chains soluble in D5)
relative to the weight of the polymer.

The characteristics of the polymer and of the
particles formed by the said polymer are as follows:

- dry extract: 50% in decamethylcyclopentasiloxane,
25 performed by thermal balance
- glass transition: 12°C by Mettler DSC
- particle size: 170 nm with polydispersity of 0.04,

performed on a Malvern Autosizer Lo-C at 25°C.

Example 3:

This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by
5 polymerization of methyl acrylate, acrylic acid and the macromonomer corresponding to a polyethylene/polybutylene copolymer (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 14 g
10 of methyl acrylate, 10 g of acrylic acid, 16 g of macromonomer of the polyethylene/polybutylene copolymer type (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

15 The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating
20 with stirring is continued for a further 15 minutes, and a mixture consisting of 70 g of methyl acrylate, 90 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour.

Next, the mixture is heated for 4 hours at
25 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of

polymer thus prepared in isododecane.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass M_w = not characterizable by GPC
- number-average molecular mass M_n = not characterizable by GPC
- polydispersity index (M_w/M_n) = not characterizable by GPC
- theoretical dry extract: 53.6% in isododecane
- particle size: not measured.

The grafted polymer comprises 8% by weight of macromonomer relative to the weight of the polymer.

- After the stability protocol has been implemented in accordance with Example 1, the dispersion obtained is found to be stable.

Example 4:

- This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and the macromonomer corresponding to a polyethylene/polybutylene copolymer with methacrylate end groups (Kraton L-1253).

- 200 g of heptane, 200 g of isododecane, 28 g of methyl acrylate, 12 g of macromonomer of the polyethylene/polybutylene copolymer type with

methacrylate end groups (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 150 g of methyl acrylate, 10 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour.

Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of polymer thus prepared in isododecane.

The grafted polymer comprises 6% by weight of macromonomer relative to the weight of the polymer.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass M_w = 143 639
- number-average molecular mass M_n = 23 965
- polydispersity index (M_w/M_n) = 5.99
- theoretical dry extract: 51.3% in isododecane
- particle size: 48 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

After the stability protocol has been implemented in accordance with Example 1, the dispersion obtained is found to be stable.

Example 5:

5 This example, which does not form part of the invention, illustrates the preparation of a polymer forming a dispersion of particles in a silicone oil, the said polymer being obtained by polymerization of methyl acrylate and a monomethacryloyloxypropyl
10 polydimethylsiloxane macromonomer having a weight-average molecular weight of 5000, sold under the name MCR-M17 by Gelest Inc.

200 g of heptane, 200 g of decamethylcyclopentasiloxane, 30 g of methyl acrylate,
15 10 g of monomethacryloyloxypropyl polydimethylsiloxane MCR-M17 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated to 90°C over 1 hour. After 15 minutes at 90°C, a change is
20 observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 160 g of methyl acrylate and 2 g of Trigonox 21S is then
25 added dropwise over 1 hour. Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium.

The outcome of this distillation operation is a stable dispersion of particles of polymer thus prepared in decamethylcyclopentasiloxane (D5).

The grafted polymer comprises 5% by weight of macromonomer (and hence of side chains soluble in D5) relative to the weight of the polymer.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass $M_w = 102\,347$
- 10 - number-average molecular mass $M_n = 28\,283$
- polydispersity index (M_w/M_n) = 3.62
- dry extract: 51.4% in D5, performed by thermal balance
- glass transition: 12°C by Mettler DSC
- 15 - particle size: 160 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

After the stability protocol has been implemented in accordance with Example 1, the dispersion is found to be stable.

20 **Example 6:**

This example, which does not form part of the invention, illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by

25 polymerization of methyl acrylate and the macromonomer corresponding to a polyethylene/polybutylene copolymer with methacrylate end groups (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 28 g of methyl acrylate, 12 g of macromonomer of the polyethylene/polybutylene copolymer type with methacrylate end groups (Kraton L-1253) and 3.2 g of
5 tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the
10 appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 160 g of methyl acrylate and 2 g of Trigonox 21S is then added dropwise over
15 1 hour.

Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of
20 polymer thus prepared in isododecane.

The grafted polymer comprises 6% by weight of macromonomer relative to the weight of the polymer.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- 25 - weight-average molecular mass $M_w = 119\ 212$
- number-average molecular mass $M_n = 31\ 896$
- polydispersity index (M_w/M_n) = 3.74

- glass transition: 10°C by Mettler DSC
 - dry extract: 49.8% in isododecane, carried out by thermal balance
 - particle size: 46 nm with polydispersity of 0.05,
- 5 performed on a Malvern Autosizer Lo-C at 25°C.

After the stability protocol has been implemented in accordance with Example 1, the dispersion obtained is found to be stable.

The polymers of Examples 1 to 6 comprise the
 10 following monomers, their amounts being indicated as a percentage by weight of the polymer:

Polymer	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Methyl acrylate	72	73	42	89	95	94
Acrylic acid	20	20	50	5	0	0
Carbon-based macromonomer	8	-	8	6	-	6
Silicone-based macromonomer	-	7	-	-	5	-

Examples 7 to 12:

15 4 inventive foundations (Examples 7 to 10)
 and 2 non-inventive foundations (Examples 11 and 12)
 were prepared, having the following compositions (the
 amounts are indicated as a percentage relative to the
 total weight of the composition):

Examples	7	8	9	10	11	12
Abil EM 97	1.8	1.8	1.8	1.8	1.8	1.8
Imwitor 780 K	0.6	0.6	0.6	0.6	0.6	0.6
Isododecane	20.38	22.10	20.28	20.11	22.10	20.33
D5	10	7.9	10	10	7.95	10
Grafted polymer dispersion	Ex. 1 3.82	Ex. 2 4.20	Ex. 3 3.92	Ex. 4 4.09	Ex. 5 4.15	Ex. 6 3.87
Pigments	10	10	10	10	10	10
Silicone gum	3	3	3	3	3	3
Nylon powder	8	8	8	8	8	8
Water	41.4	41.4	41.4	41.4	41.4	41.4
Preservative	0.3	0.3	0.3	0.3	0.3	0.3
Magnesium sulfate	0.7	0.7	0.7	0.7	0.7	0.7

Each composition contains 2.1% by weight of active grafted polymer substance.

5 Ingredients used:

ABIL EM 97: α,ω -substituted, ethoxylated propoxylated silicone/cyclomethicone (85/15) blend, sold by the Goldschmidt Company

Imwitor 780 K: mono- and diglycerides of isostearic acid esterified with succinic acid sold by the Sasol Company

D5: cyclopentasiloxane

Silicone gum: blend of polydiphenyl dimethylsiloxane and cyclopentasiloxane (15/85) sold under the name

15 Mirasil C (DPDM by Rhodia)

Nylon powder sold under the name Orgasol® 2002 extra

D NAT COS by Atofina

the 10% of pigments comprise:

1.43% of yellow iron oxides coated with triisopropyl
isostearoyl titanate (BYO-I 2 from Kobo)

0.46% of brown iron oxides coated with triisopropyl
5 isostearoyl titanate (BRO-I 2 from Kobo)

0.22% of black iron oxides coated with triisopropyl
isostearoyl titanate (BBO-I 2 from Kobo)

7.89% of titanium dioxide coated with triisopropyl
isostearoyl titanate (BTD-401 from Kobo)

10 Thereafter the transfer index of each
composition was measured in the presence of sebum in
accordance with the following measurement protocol:

 A substrate (square of 40 mm × 40 mm)
composed of a layer of neoprene foam which is adhesive
15 on one of its faces (sold under the name RE70X40 212B
from Joint Technique Lyonnais Ind) is prepared. An
adhesive crown having an internal diameter of 24 mm and
a thickness of approximately 250 µm is affixed to the
non-adhesive face of the substrate. The composition is
20 applied inside the crown and is levelled off with a
glass slide so as to give a deposit of the composition
approximately 250 µm thick, and then the crown is
withdrawn and the deposit is left to dry in an oven at
37°C for 20 hours.

25 The substrate is subsequently bonded by its
adhesive face to an endpiece with a diameter of 27 mm
which is fixed on a press (Statif Manuel SV-1 from

Imada Co. Ltd.) which is equipped with a dynamometer (DPS-5R from Imada Co. Ltd.)

On a piece of photo-quality coated paper (reference Epson S041061, 102 g/m²) a strip is drawn
5 which is 4 cm wide and 21 cm long, and within this strip 5 boxes each 4.2 cm long are drawn along the longitudinal axis of the strip. The paper is placed on the bed of the press.

In the centre of the first box a drop of
10 10 µl of artificial sebum is deposited, which has the following composition:

- triolein	29%
- oleic acid	28.5%
- oleyl oleate	18.5%
15 - squalene	14%
- cholesterol	7%
- cholesteryl palmitate	3%

The substrate (comprising the sample of composition) is then pressed onto the first box of the
20 paper strip, with a force of approximately 4 kg exerted for 5 seconds. The paper is then displaced in a regular, rectilinear fashion over the entire length of the strip, in such a way that the substrate is in contact with the entire length of the strip. The speed
25 of displacement of the strip is of the order of 10 cm/s.

The trail of product deposited on the paper

strip is then observed visually. A grade ranging from 0 to 5 in increments of 0.5 is awarded as a function of the number of boxes, from the first to the fifth, which have been traversed, where appropriate, completely or
5 partly by the trail of product.

For certain products, without coloration, a visualization step may be necessary in order to make the trail of product visible. By way of example, a compound is used which is able to produce a coloured
10 reaction on contact with the transferred product. According to another example, an active which emits in the visible range at least some of a UV radiation (Wood lamp) is incorporated into the product under test.

Grade 5 is awarded when, by observation,
15 after the relative displacement between paper and substrate has taken place, there is substantially no product (less than 10%) remaining on the substrate. In this case, the transfer may be termed total.

Grade 5 is also awarded when the trail of
20 product extends beyond the fifth box, independently of the amount of product remaining on the substrate.

Grade 0 is awarded when no product present on the support is transferred to the strip of paper. No visible trace can be observed on the sheet. The
25 transfer may be termed zero.

By convention, the line of separation between box n and box $n+1$ forms part of box n .

The table below illustrates the way in which the other grades are awarded as a function of the point in boxes 1 to 5 at which the trail of product ends. For these grades, a larger or smaller amount of product remains on the substrate. The transfer is partial.

No. of the box at which the trail of product stops	Grade	
	More than half of the box	Up to half of the box
5	4.5	
		4
4	3.5	
		3
3	2.5	
		2
2	1.5	
		1
1	0.5	

The results obtained were as follows:

Compositions in which the grafted polymer comprises a carbon-based macromonomer:

Example	7	9	10	12
Transfer index	0.5	0.5	3.5	4.5

It is found that, for the compositions containing a grafted polymer comprising a carbon-based macromonomer (Examples 7, 9, 10 and 12), the

compositions of Examples 7, 9 and 10 according to the invention - for which the grafted polymer comprises acrylic acid - form a deposit having a transfer index (of 0.5, 0.5 and 3.5, respectively) which is lower than
5 that of the deposit formed with the composition of Example 12, which does not form part of the invention (since the grafted polymer does not contain acrylic acid) and whose transfer index is 4.5.

Compositions for which the grafted polymer
10 comprises a silicone-based macromonomer:

Example	8	11
Transfer index	0.5	3.5

For the compositions containing a grafted polymer comprising a silicone-based macromonomer
15 (Examples 8 and 11), the composition of Example 2 according to the invention - for which the grafted polymer comprises acrylic acid - forms a deposit having a transfer index of 0.5, which is lower than the index of 3.5 obtained for the deposit formed with the
20 composition of Example 12, which does not form part of the invention.

It is also observed that the compositions of Examples 7, 8 and 9 according to the invention exhibit the best non-transfer properties (index of 0.5),
25 effectively confirming that the presence of acrylic acid, in particular at a level of 20% and of 50% in the

grafted polymer, contributes to the desired non-transfer property.

Example 13:

A mascara is prepared whose composition is as follows:

Phase A	
Candelilla wax	15%
Stearic acid	5.8%
Polymer dispersion of Example 4	10%
Phase B	
Triethanolamine	2.9%
Hydroxyethylcellulose	0.9%
Gum arabic	3.5%
Black iron oxide	8%
Preservatives	qs %
Water	qs 100

This composition may be prepared in a standard manner by hot formation of a wax-in-water emulsion.

The fatty phase (phase A) containing the wax and the stearic acid is heated until the mixture of constituents has melted completely. Subsequently the polymer dispersion of Example 2 and the pigments are incorporated with stirring into the oily phase. In parallel, the aqueous phase (phase B), containing the neutralizing agent (triethanolamine), and the gelling polymers are brought to a temperature at least equal to the temperature of the fatty phase. The aqueous phase

is subsequently added to the oily phase, with vigorous stirring (3000 rpm), for hot formation of the emulsion. Stirring and the temperature are maintained for approximately 30 minutes.

5 Moderate paddle stirring is then applied until the composition has returned to ambient temperature.

Example 14:

A lipstick was prepared whose composition was
10 as follows:

	- Hydrogenated polyisobutene (Parleam oil)	5.2 g
	- Poly(12-hydroxystearic acid) stearate (Octacare DSPOL300 from Avecia)	0.2 g
15	- Sucrose acetate isobutyrate (Eastman SAIB from Eastman Chemical)	5 g
	- Mixture (80/20) of C30-C50 fatty alcohols and C30-C50 hydrocarbon (Performacol 550 from New Phase technologies)	2 g
	- Pigments	8.2 g
20	- Polyethylene wax (Performalene 500 polyethylene from New Phase technologies)	10 g
	- Polymer dispersion of Example 4	68.82 g
	- Perfume	qs

The Parleam oil, poly(12-hydroxystearic acid)
25 stearate and sucrose acetate isobutyrate are mixed with heating at approximately 60°C. This mixture is used to produce a pigment millbase, by passing the mixture 3

times through a triple-roll mill.

The pigment millbase and the polyethylene wax are then mixed, with heating at 100°C. Thereafter the polymer dispersion is added with stirring, followed by
5 the perfume.

The formula is poured at 42°C into a mould and then placed in a freezer. The resulting stick is subsequently demoulded.

This lipstick allows a makeup result to be
10 obtained that exhibits good transfer resistance.